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# Emulsifying Properties of Dextran Derived Polymers

Xiying Zhang

*Worcester Polytechnic Institute*

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# Emulsifying Properties of Dextran Derived Polymers

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A Major Qualifying Report  
Submitted to the Faculty of  
Worcester Polytechnic Institute

In Partial Fulfillment of the Requirement  
for a Bachelor of Science Degree  
in the Field of Chemical Engineering

By:

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Xiying Zhang

Approved by:

---

Professor Terri Camesano, Advisor (WPI)

---

Professor Alain Durand, Co-Advisor (ENSIC)

Date: April 28, 2011

## Acknowledgements

I would like to first thank our advisors Professor Terri Camesano and Professor Alain Durand for working with us so closely on the project – providing their guidance and support through my stay in Nancy, France – and also for taking the time to get to know me as an individual.

Much appreciation goes to Maxime Laville, Marie Blanchard, Marie-Christine Grassiot and Joanna for their technical support, translation services, and helping us adapt to the French culture.

Last but not least, I extend very special thanks to our school for offering me this great opportunity to work in a state-of-art facility overseas in France.

## Abstract

The amphiphilic dextran derivatives have been shown to become convenient drug vehicles.<sup>6-9</sup> However, the solution behavior and the surface-active properties vary with different modified dextran polymers. This project was conducted at Laboratoire de Chimie Physique Macromoléculaire (LCPM) of Ecole Nationale Supérieure des Industries Chimiques (ENSIC) in conjunction with Worcester Polytechnic Institute (WPI). The experimental objective was to investigate the aqueous medium behavior and surface-active properties of native dextran and its derivatives. Experimental variables such as concentration, modification process, chemical structure, and time were examined. The viscosity data of native dextran and modified dextran derivatives were collected for studying the solution behavior in aqueous media. Optimization techniques such as obtaining significant detectable effect of polymeric surfactant by extending the holding time, running water circulation at 25°C, and the use of drying oven were all applied to improve the efficacy and the accuracy of the system. Different modification process of the polymeric surfactant led to the different surface-active properties. Recommendations were made for the improvement of the experimental procedures as well as the future work continuing the project study.

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## Executive Summary

Nanotechnology, both evolutionary and revolutionary, is the engineering and manufacturing process at macro scale in an atomic or a molecular manner.<sup>4</sup> The application of the nanotechnology in drug delivery systems is expected to play a key role in the stage of modern pharmaceutical and biotechnology industries.

A desirable drug delivery system should have the capabilities of the control over the release of drugs, targeted delivery of drugs in a cell- or tissue-specific manner<sup>4</sup>, and biocompatibility with the host system. Most of these drug vehicles are polymers like chitosan, inulin, pectin and others.<sup>17-30</sup> However, the modified polysaccharides based on native dextran have caught considerable attention for its suitable application as a biomaterial used for the parental administration of drugs.

The research group in ENSIC have devoted considerable attention and efforts in exploring for the viable drug carriers, and most of their studies focused on modified polysaccharides based on native dextran. Dextran derivatives have been shown to meet the important parameters for the successful development and manufacturing of targeted drug delivery vehicles.<sup>6-11, 15, 36, 43, 44</sup> Dextran and its derivatives are biocompatible materials with the core materials and the encapsulating molecule. These polymers were also found to be efficient emulsifying stabilizers in the colloidal systems. In addition, dextran is an economically friendly biomaterial which could be developed to scalable unit operations of mass production used in the clinical trials.

The objective of this project study was to evaluate the emulsifying properties of various dextran derivatives DexC10<sub>x</sub> as well as the native dextran T40 and compare their solution behavior in aqueous medium and surface-active properties. In order to fulfill this objective, two experimental tasks were assigned:

- To compute corresponding Huggins' constant of native dextran and DexC10<sub>7</sub> for the investigation on their solution behavior in aqueous medium;
- To measure the surface / interfacial tension forces of several different modified dextran polymers for the evaluation of their surface-active properties.

The values of Huggins' constant for both native dextran and DexC10<sub>7</sub> were in good agreement with the theory explained in a previous study.<sup>9</sup> Generally, Huggins' constant should be around 0.4 for non-interacting macromolecules in good solvent, and it can reach above 5 for highly interacting macromolecules. In the experimental tests, native dextran solution was the non-interacting macromolecules in good solvent (pure water), and DexC10<sub>7</sub> was the highly interacting macromolecule.

The surface-active properties were tested by air-water interfacial tension and oil-water interfacial tension. In general, the surface / interfacial tension force plotted against the concentration would show the generic trend of the polymers: the trend line was flat at both high concentrations and low concentrations; however, the plot was much steeper in between which indicated a significant tension force drop over the concentration. Overall, native dextran and dextran derivatives all followed the predicted model.

Notably, the interfacial tension forces of DexC10<sub>10</sub> (n°1) was very similar to that of DexC10<sub>7</sub> which meant with the same modification process (freeze-drying) and close values of the substitution ratio of the glucose groups, the two polymers behaved similarly. However, even DexC10<sub>10</sub> (n°1) and DexC10<sub>10</sub> (n°2) were identical polymers in terms of chemical structure. DexC10<sub>10</sub> (n°2) was found to be less surface active due to the different modification process (biphasic medium dispersion).

Another interesting finding was the induction period of the diluted polymer solutions. In order to detect significant effect of the polymeric surfactants, the induction period was extended to an hour for the diluted solution (< 1 g/L). This longer induction period for solution of low concentration might be due to the high hydrophobicity of the C10 group which easily led to the formation of polymeric aggregates.<sup>9</sup>

The ultimate goal of developing dextran derivatives as drug carrier surface was to relate the oil-in-water interfacial tension to the chemical structure. To continue this project study, a droplet sizing experiment mission was suggested to investigate further into the oil-in-water emulsion stability of the polymers. Moreover, the surface characteristics should also be identified in order to develop these polymers in creating colloidal systems.

## Introduction

Nanotechnology has been used extensively in various fields such as cosmetics<sup>38</sup>, agriculture<sup>1</sup>, pharmaceutical<sup>4</sup>, and medical therapeutics<sup>1</sup>. It is in people's everyday life during modern age. However, the application of nanotechnology, both evolutionary and revolutionary, will clearly change the landscape of the drug delivery system field.<sup>4</sup>

A series of nanomaterials have been introduced to drug delivery to develop effective drug carriers. Since cellulose ethers added by long-chain *n*-alkyl epoxides were proposed as nonionic water-soluble polymeric surfactants in 1982, the majority of polymeric surfactants had been prepared by hydrophobic modification of polysaccharides.<sup>5-6</sup> Numerous of polymers have been suggested and tested as potential drug carriers since then.<sup>17-30</sup> The parameters of cytotoxicity, biocompatibility, biodegradability as well as the polymer stability are the major concerns when considering the polymer as a carrier surface.<sup>40</sup>

In the search of new materials to obtain nanoparticles, the dextran derivatives was found to be great candidates with the desirable features. Dextran derivatives are highly soluble in water, biocompatible in the colloidal system, and biodegradable.<sup>41</sup> The LCPM research group have been studying dextran derived polymers in the following fields: drug delivery, emulsion stabilization, and miniemulsion polymerization.<sup>7</sup> In the past fifteen years, the research group have evaluated a series of dextran derivatives for surface characteristics, emulsifying properties, and structural modifications.<sup>6-11</sup> However, the surface-active behavior varies given different dextran derivatives. The experimental task

of this study is to test several different types of dextran derivatives using the existing protocols and data analysis.

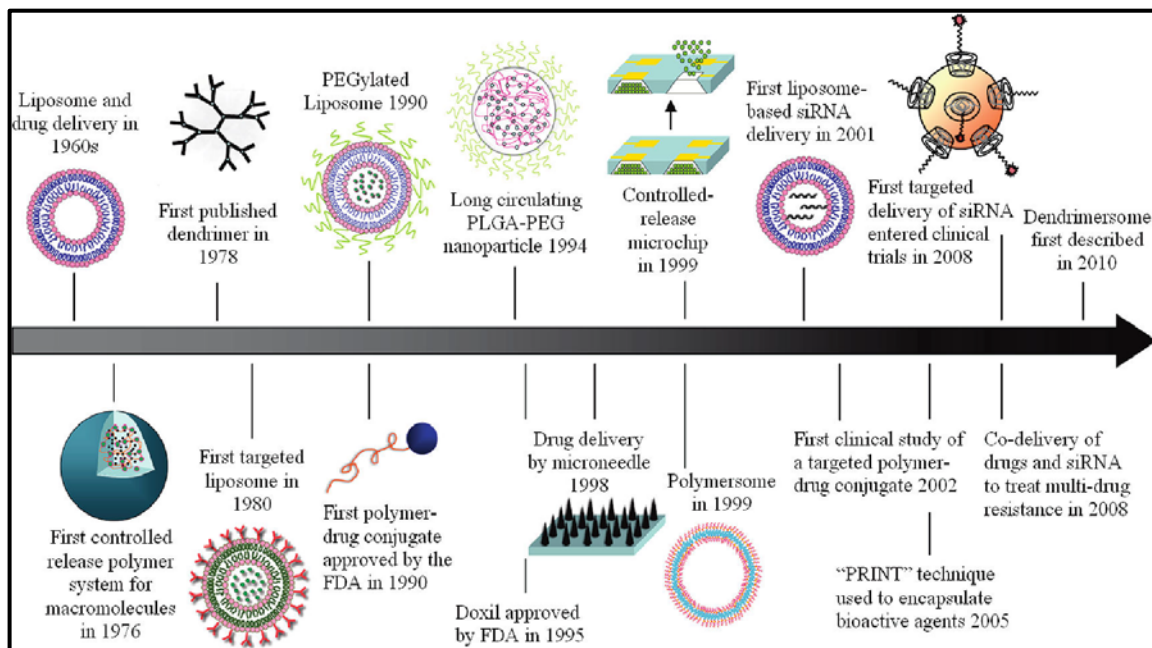


Figure 1: Development of Drug Delivery System<sup>4</sup>

## Drug Delivery System

Drug delivery systems are lipid- or polymer- based nanoparticles serving as the particulate carriers of conventional drugs.<sup>12</sup> Since the liposome was introduced to the small scale drug delivery system for parental (intravenous) applications in 1960s, considerable attention and work have been devoted to exploit drug delivery system for parental administration of drugs (Figure 1).<sup>12-13</sup>

There have been a variety of organic and inorganic biomaterials proposed and prepared for drug delivery. Up to date, there are over twenty nanotechnology therapeutic products that have been approved for clinical use.<sup>4</sup> In drug delivery system field, the

emerging nanotechnology have given people the opportunity of better delivery of drugs with low water solubility, targeted drug delivery specified in a cell- or tissue- accuracy, and co-delivery with two or more drugs.<sup>4</sup> The intrinsic complexity in the manufacturing process will most likely lead to a barrier for pharmaceutical companies to make equivalent drug delivery system drastically.<sup>4</sup> Regardless, given the arbitrary reasons, nanotechnology application in drug delivery still has a promising future.

### **Polymeric Surfactants**

General applications of polymeric surfactants include dyestuffs, paper coatings, inks, agrochemicals, pharmaceuticals, personal care products, ceramics and detergents.<sup>16</sup> However, polymeric surfactants play an essential role in the preparation of oil-in-water (O/W) and water-in-oil (W/O) emulsion and dispersion systems. Polymeric surfactants offer many performance advantages over traditional surfactants, especially in the challenging parental administration of drugs, which can be prone to physical instability. It has been decades since the liposome polymer was developed to a viable nonionic surfactants.<sup>5</sup>

### **Dextran Derived Polymers**

Polymeric drug delivery systems are expected to change the landscape of the pharmaceutical drugs and medical therapeutics in the foreseeable future. Much attention has given to the chemical modification of different polysaccharides like pullulan<sup>17-19</sup>, chitosan<sup>20-22</sup>, inulin<sup>23</sup>, pectin<sup>24-26</sup>, hyaluronate<sup>27</sup> and others<sup>28-30</sup>. However, modified dextran polymers were proved to be very convenient for pharmaceutical applications.<sup>3</sup>

At LCPM in Nancy, France, the research group have been devoted considerable efforts in developing various dextran derived polymers by manipulating the attached functional groups of dextran T40.<sup>6-11, 15</sup> Dextran chains exhibit good stability in the colloidal system at either large ionic forces or low concentrations.<sup>42</sup> Additionally, dextran derivatives attached with functional groups (such as phenoxy, epoxy groups) are biocompatible with the core materials and the encapsulating molecule.<sup>43</sup> Dextran and its derivatives are also biodegradable and economic friendly.<sup>43</sup> Therefore, amphiphilic dextran derivatives can be adequate carrier for drug delivery systems.



## Background

### Dextran and Dextran Derived Polymers

Given the favorable therapeutic applications and convenient modification, dextran has often been developed to prepare dispersion systems.<sup>10</sup> Native dextran is usually modified by attaching the aromatic group on the polymeric backbone.<sup>3</sup>

### Native Dextran

Native dextran (T40), a polymer of glucose, is an odorless white powder.<sup>2</sup> It is mainly comprised of  $\alpha$ -D-(1 $\rightarrow$ 6) linked glucose units and some short  $\alpha$ -D-(1 $\rightarrow$ 3)-lined glucose branch units (Figure 2). In the manufacturing process, dextran is acquired by the fermentation of sugar beet sucrose with *Leuconostoc mesenteroides*, a bacterium in the *Lactobacillus* family.<sup>31</sup> The raw dextran product is a viscous syrup after the filtration, and this syrup can either be dried to get product powder or diluted to a stable syrup solution.<sup>31</sup> Dextran is a versatile chemical used extensively not only in the nanotechnology but also in the waste-water management (flocculation), photographic, and agricultural industries. Dextran offers many useful features such as stability under room temperature, biodegradable compound, and economical starting material.

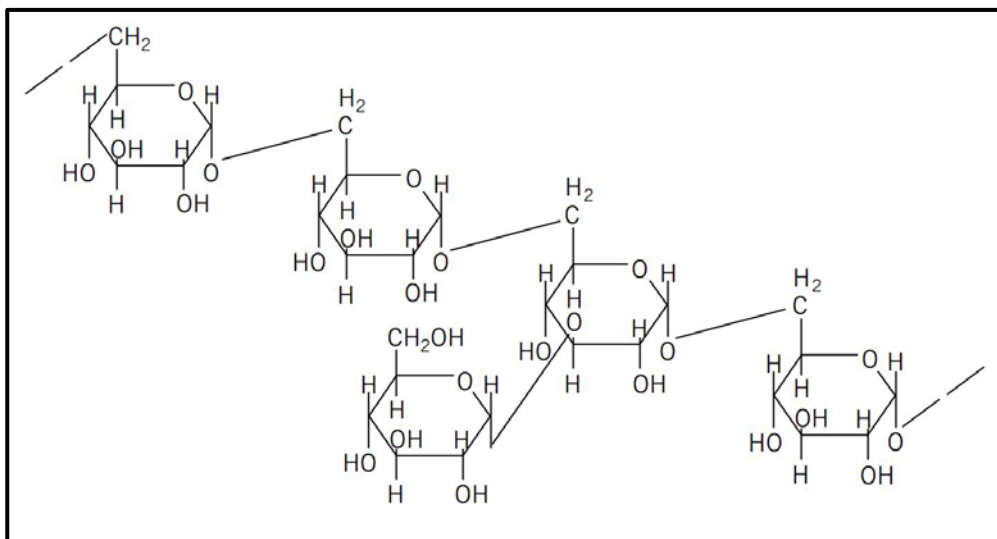


Figure 2: Structure of Fragment of Native Dextran Molecule<sup>36</sup>

The desirable characteristics of this neutral bacterial polysaccharide gave the convenience of both the function group modification and practical applications.<sup>7</sup> The amphiphilic dextran derivatives are mostly prepared from dextran T1-T500.<sup>2</sup> The dextran used in the study was acquired from Pharmacia, and the amphiphilic dextran derivatives were prepared based on T40. The molar mass of T40 was found to be  $\bar{M}_n = 26,000$  g/mol, and  $\bar{M}_w = 40,000$  g/mol by LCPM.

### Modified Dextrans

Dextran can be easily modified by manipulating the attached functional group to achieve favorable physical properties. The study used DexC10x derived from native dextran T40. The modification process can happen either in dimethylsulfoxide (DMSO) or in water.<sup>3</sup>

For the modification in water, 10 g of native dextran T40 were mixed with 1,2 epoxy-3- phenoxypropane in 1 M NaOH solution at the ambient temperature of 25 °C for 48 hours. This intermediate product would then go through a double precipitation with ethanol, and a dialysis against deionized water for 24 hours, and freeze-dried.<sup>46</sup>

The synthesis of the dextran carried on in DMSO was similar as the one in water. 3 g of native dextran T40 were dissolved in 54 mL of an aqueous solution of tetrabutyl ammonium hydroxide (27 %, w/w) for an hour. The crude product was then freeze-dried and the powder was dissolved in 120 mL DMSO. 1,2-epoxy-3-phenoxypropane, 1,2-epoxy octane or 1,2-epoxydodecane were mixed in the solution after 24 hours. The reaction took four days under ambient environment. The intermediate product were dialyzed against water/ethanol (50/50, v/v) and water, and eventually freeze-dried.<sup>36</sup>

On the macroscale, the attachment of the aromatic or aliphatic hydrocarbon groups onto the glucose units was achieved by reacting dextran with epoxides in a basic medium (NaOH)<sup>9</sup> (Figure 3).

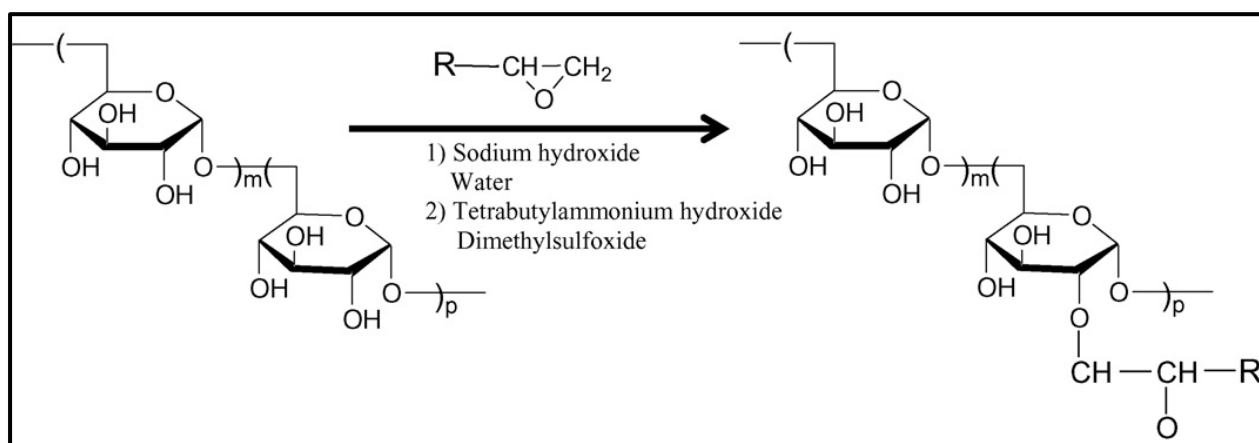


Figure 3: Modification Process of Dextran

The dextran derivatives have different notations including DexP<sub>τ</sub>, DexC6<sub>τ</sub>, and DexC10<sub>τ</sub> corresponding to the nature of the attached functional groups: phenoxy, n-C<sub>6</sub>H<sub>13</sub>- (C6), and n-C<sub>10</sub>H<sub>21</sub>- (C10). The Greek letter “τ” represents the substitution percentage of modified glucose units, and it is also called the degree of hydrophobic modification, and it is defined by  $\tau = 100 \times y/(x+y)$ .<sup>9</sup> (Figure 4) τ sometimes could be replaced by other letters like “x” or “γ”. To simplify, τ is replaced by x in the project study report.

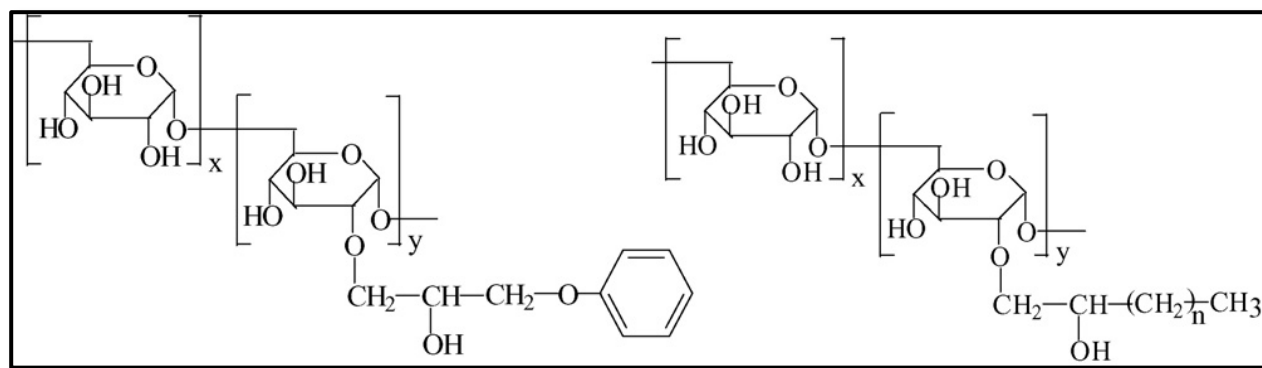


Figure 4: Schematic of repeating Units of DexP<sub>τ</sub> (left), DexC6<sub>τ</sub> and DexC10<sub>τ</sub> (right, n = 5 and 9, respectively)

## Emulsion Science

To transport oil soluble materials (in a non-viscous form), droplets of oil-in-water can be utilized and eventually to release them on the targeted destination. Medical therapeutics, ice cream, ink are frequently based on these “emulsions”. By definition, emulsion is a system consisting of a liquid dispersed with or without an emulsifier in an immiscible liquid usually in droplets of larger than colloidal size. One most common example would be milk, which is an oil-in-water emulsion.<sup>16</sup>

### Emulsion Formation and Characterization

Simply speaking, emulsions are generally made of two immiscible fluids, one being dispersed in the other with the presence of the emulsifier (Figure 5).<sup>48</sup> In order to form the emulsion, in other words, to disperse two immiscible liquids, the surface-active agent must be present. Besides the formation of the emulsion, the importance of the emulsifier is on its long-term stability.<sup>49</sup>

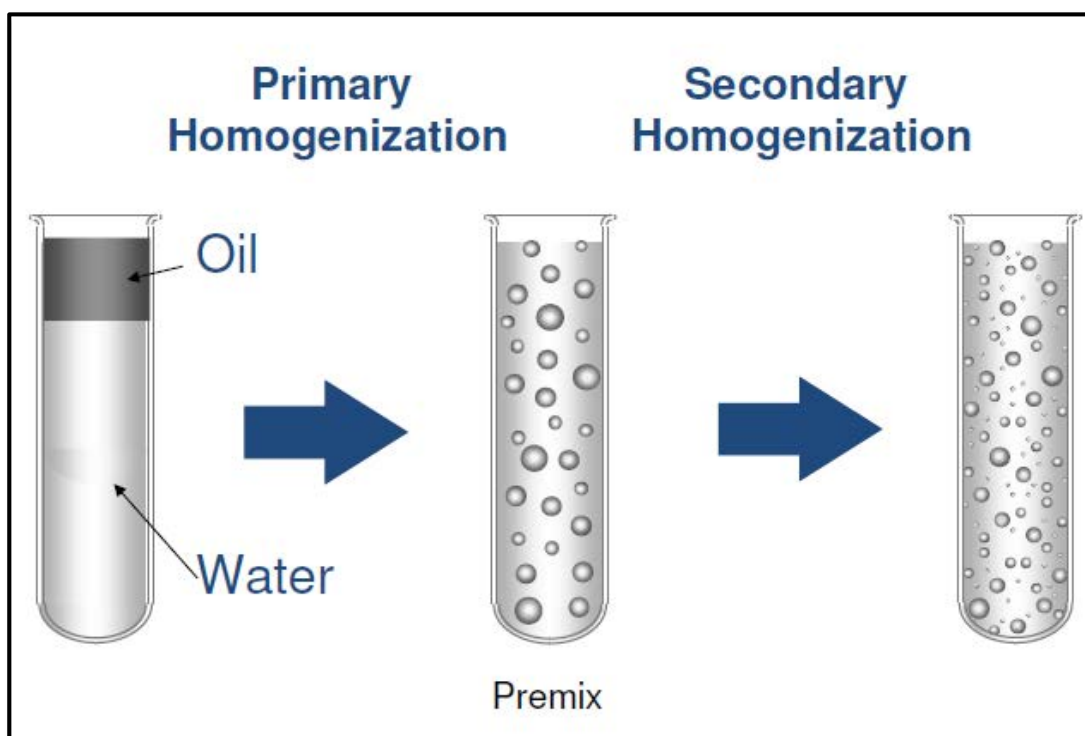


Figure 5: Principle of Emulsion Formation

There are several categories of emulsions according to the emulsifier or the structure of the system (Figure 6).

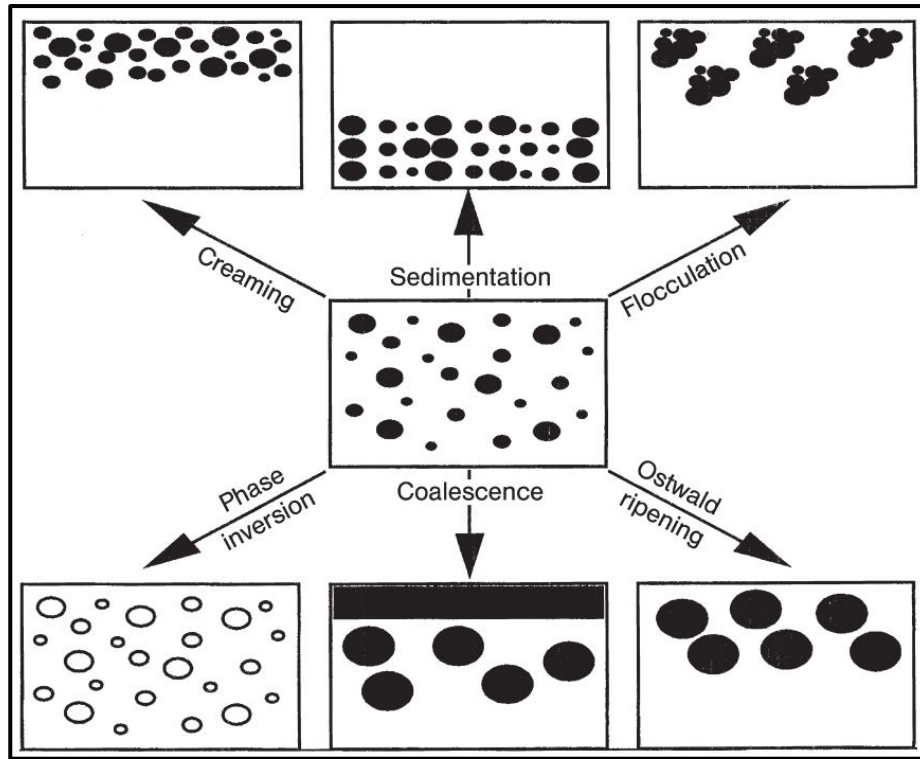


Figure 6: Breakdown Processes in Emulsions<sup>48</sup>

### Ostwald Ripening and Coalescence

There are two distinct breaking mechanisms of emulsions. One, called Ostwald ripening, is also referred to as molecular diffusion<sup>32</sup> or isothermal distillation<sup>33</sup> in the literature. The other mechanism, called coalescence, could cause a total destruction in the end.

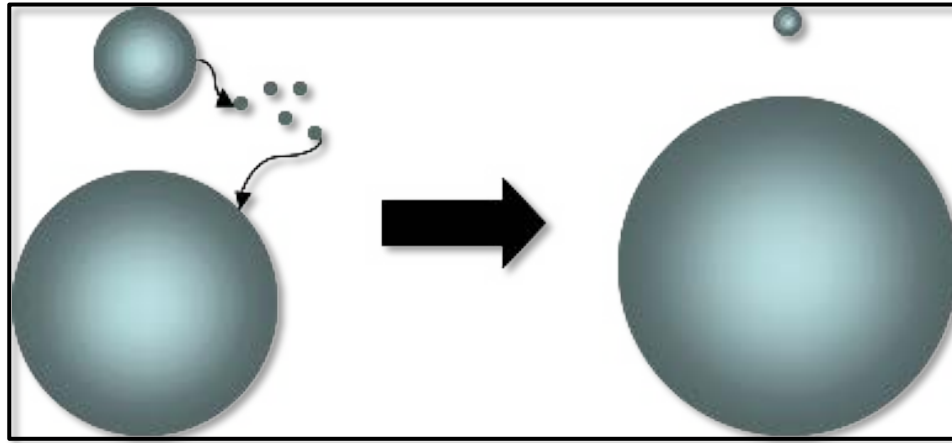


Figure 7: Basic Schematic of the Ostwald Ripening Process<sup>47</sup>

Ostwald ripening is due to the difference in chemical potential of the material within the droplets. It is the expansion of one emulsion droplet at the expense of a smaller one. Alternatively, Ostwald ripening can be considered as a process of, by decreasing the interfacial area, the free energy of the system is also reduced. Overall the effect is an increase in the average radius of the emulsion droplets with time as the smaller droplets dissolve and joined the larger droplets. Figure 7 shows a simplified schematic of the Ostwald ripening process.

Coalescence usually refers to the fusion of two or more droplets to form larger droplets. This process is due to the thinning and disruption of the liquid film between the droplets.<sup>49</sup> If the emulsion system is separated completely into two discrete liquid phases. The surface or film fluctuations drive the process. However, this driving force also results in a close distance where the van der Waals forces are strong and balances the separation force out.<sup>49</sup>

## Surface and Interfacial Tension

In 1894, van der Waals proposed the monumental theory of the surface tension of liquids, which has been extended by Cahn and Hilliard.<sup>51</sup> Interfacial tension is similar to surface tension because of the cohesive forces. However, the major forces engaged are adhesive tension forces between the two distinct phases (gas/liquid, liquid/liquid, gas/solid, or liquid/solid). The interfacial tension is the result of the cohesive energy (force) at an interface due to the imbalance of forces between molecules and an interface, which can be quantified as a force measurement.<sup>51</sup>

If one of the phases is a gas phase, the interfacial tension is generally referred to as the surface tension. However, in either case, the phase with the higher density is called “heavy phase”, and the phase with the lower density is called the “light phase”.<sup>51</sup>

## Viscosity

The solution behavior of the polymeric surfactants are usually investigated by viscometric experiments. The specific viscosity,  $\eta_{sp}$ , is increasing with solution concentration. The relationship follows a polynomial equation:

$\eta_{sp} = C[\eta](1 + k_1C[\eta] + k_2(C[\eta])^2 + k_3(C[\eta])^3 + \dots)$ , where  $k_1, k_2 = (k_1)^2/2!, k_3 = (k_1)^3/3!, \dots$  are constants obtained through experiments.<sup>9</sup>  $C$  = concentration, g/L, and  $[\eta]$  = intrinsic viscosity of the polymer, L/g. This polynomial equation is the development of the usual Huggins' equation used for the dilute solutions and it is:

$$\eta_{sp} = C[\eta] + k_H[\eta]^2C^2$$



$k_H$  = Huggins' constant. Huggins' constant is around 0.5 for the native dextran T40 in water, and it could reach a very high value for modified dextrans such as 7 for DexC10<sub>11</sub>.<sup>9</sup> However, the Huggins' constant are not predictable for dextran derivatives even given the attached group and substitution ratio (Figure 8).

Viscometric results obtained with dextran derivatives, in aqueous medium at 25 °C

Polymer	Solvent	$[\eta]$ (mL/g)	$k_H$	$C_{lim}$ (g/L) <sup>a</sup>
T40 <sup>®</sup>	Water	20.0	0.55	60
DexP <sub>15</sub>	Water	14.0	0.95	–
DexC <sub>612</sub>	Water	16.8	1.13	55
	0.1 M NaCl	10.9	4.25	35
DexC10 <sub>11</sub>	Water	8.1	6.98	38
DexP <sub>23</sub>	Water	9.7	3.2	–
	0.1 M NaCl	9.6	3.5	–
DexP <sub>31</sub>	Water	7.4	6.20	–
DexC <sub>638</sub>	Water	8.0	3.65	48
DexC10 <sub>31</sub>	Water	11.2	0.28	~33 <sup>b</sup>

Figure 8: Huggins' Constant of Various Dextran Derivatives<sup>9</sup>

## Equipment

### Tensiometer

To measure the surface and interfacial tension force, a tensiometer was used. It is a time-proven instrument for accurate and reproducible measurements. EasyDyne can be used for measurements of the surface tension of liquids, the interfacial tension between two liquids and the density of a liquid. The machine can operate within the temperature range between -10 °C and 130 °C. A Du Noüy Ring is be used as the measuring probe for experiments.

There are a few advantages for using the ring method, including:

- Many international standards for surface and interfacial tension measurements are still based on the ring method;
- Many values in the literature have been obtained with the ring method. This means that in many cases the ring method should be preferred for comparison purposes;
- The wetted length of the ring exceeds that of the plate by the factor of 3. This leads to a higher force on the balance and accordingly to a better accuracy. This effect does not influence the results of surface tension measurements, but small interfacial tensions can be carried out more accurately with the ring method;
- Some substances, e.g. cationic surfactants, show poor wetting properties on platinum. In such cases the surface line between a ring and the liquid is more even than that of a plate.

## Methodology

This experimental study focused on the surface-active properties of amphipathic dextran and its derivatives. To characterize and compare various polymer samples, both the viscometric properties and the surface / interfacial tension forces were examined. In identifying the properties of the sample solutions, polymers were tested at different concentrations.

## Materials

A series of solution samples were prepared for viscometry and surface/ interfacial tension experiments. However, the concentrations of sample solutions varied with various polymers. The viscometry and surface / interfacial tension experiments required different concentrations too. Besides, all the solution samples were prepared based on the mother-daughter solution preparation method.

### Native Dextran (T40)

For the viscometry tests, the concentration range of aqueous solution samples was between 5 g/L to 60 g/L with approximately 10 mL each. The mother solution samples were always prepared first, and the daughter solution samples were acquired by diluting the mother solution samples. To make the mother solution (60 g/L), 1.5 g of T40 powder was weighed in a vial, and then 25 g of filtered (through 0.45 mm filters) MilliQ (pure water) was added. Taken 15 mL of the mother solution and added 7.5 g of filtered MilliQ, the daughter solution of 40 g/L was prepared. The second daughter solution (20 g/L) were prepared by taking 10 g of the 40 g/L solution and adding 10 g of filtered MilliQ. The

following daughter solutions (10 g/L and 5 g/L) were prepared by the same mechanism. Additionally, all the T40 solutions must be stirred for at least 3 hours.

For the surface tension tests, the concentration range of aqueous solution samples was 10, 5, 2, 1, 0.1, 0.01 g/L with the 10 and 1 g/L samples being the mother solution. It was desired to have at least 20 mL of each sample.

#### **DexC10<sub>7</sub>**

For the viscometry tests, the concentration range of the aqueous solution samples was the same as that of T40. The samples were prepared at concentration of 60, 40, 20, 10 and 5 g/L. However, to save the polymers, only 5 mL of each sample was made.

For the surface and interfacial tension tests, the concentration range of aqueous solution samples was 10, 5, 2, 1, 0.1, 0.01 g/L with the 10 and 1 g/L samples being the mother solution. It was desired to have at least 20 mL of each sample.

#### **DexC10<sub>10</sub> n°1 and n°2**

DexC10<sub>10</sub> n°1 and n°2 were identical in chemical structure and substitution ratio, but the two polymers only differed in the modification process. DexC10<sub>10</sub> (n°1) was processed using freeze-drying modification process just as DexC10<sub>7</sub>, whereas DexC10<sub>10</sub> (n°2) was processed using biphasic medium method. The biphasic medium method was a novel modification process. The polymers were dissolved in a biphasic medium and the reactants were dispersed into the medium slowly. This process was also performed under ambient environment.

The viscometry was not tested for these two types of polymers. However, DexC10<sub>10</sub> n° and n°2 were characterized by tensiometer at concentrations of 1, 10<sup>-1</sup>, 10<sup>-2</sup>, 10<sup>-3</sup>, 10<sup>-4</sup> g/L.

#### DexC10<sub>5</sub>

For the viscometry tests, the concentration range of the aqueous solution samples was the same as that of T40. The samples were prepared at concentration of 60, 40, 20, 10 and 5 g/L. However, to save the polymers, only 5 mL of each sample was made.

For the surface tension tests, the concentration range of aqueous solution samples was 10, 5, 1, 10<sup>-1</sup>, 10<sup>-2</sup>, 10<sup>-3</sup>, 10<sup>-4</sup> g/L with the 10 and 1 g/L samples being the mother solution. It was desired to have at least 20 mL of each sample.

#### Viscometry

Viscosity measurements were made with an Ostwald capillary viscometer (0.46 mm diameter) in a viscometer bath (manufacture) as previously described<sup>1</sup>. It was immersed in a large water bath regulated at 25 ± 0.1 °C, and outflow times (seconds) for solution samples were measured by the computer aided system. To obtain experimental data, a 3 mL filtered sample was added to the viscometer capillary. After turning on the viscometer from the desktop end, the sample was released into the capillary tube and the time for the sample to flow through the tube was monitored. The process was repeated 8 times for each test.

The viscometer must be thoroughly washed and rinsed with distilled water (4 times) and acetone (3 times) using the vacuum. In addition, to calibrate the viscometer, the

first measurement of the viscometer should always be MilliQ water, and the target flow time should be around 45.

The time required for the solution (polymer samples,  $t$ ) and the solvent (MilliQ,  $t_0$ ) to flow through the capillary under atmospheric pressure was recorded. Data were interpreted as specific viscosity,  $\eta_{sp}$ , which was calculated in terms of flow times of solvent ( $t_0$ ) and solution ( $t$ ) by the equation:

$$\eta_{sp} = \frac{t-t_0}{t_0 \times c} \quad (1)$$

Where  $c$  is the concentration of the sample solution.

To obtain the Huggins coefficient,  $k_H$ , the specific viscosities were plotted against concentrations of the same polymer sample, and a linear trendline was added. The trendline equation and R-squared value were displayed along with it as well. The linear relationship was defined as  $y = ax + b$ , and Huggins coefficient,  $k_H$ , was calculated by the equation:

$$k_H = \frac{a}{b^2} \quad (2)$$

### Dry Extracts of the Solution

The concentrations described in materials section were ideal value. However, the actual concentration could not 100 % match the desired concentration due to the random error. Thus, the actual sample solution concentrations were obtained by drying the solution samples.

First, to make sure that the vials were completely dried, the labeled vials had to be dried in the oven for 24 hours at 80 °C. The vials were weighed with their corresponding labeled caps after empty drying ( $M_1$ , g), and they were weighed again with approximately 1 g of each solution sample without the labeled caps ( $M_2$ , g). The vials containing solution samples were then moved in the oven without caps for 24 hours at 80°C. The dried samples were weighed again in the vials as well as the caps ( $M_3$ , g). The actual concentrations were calculated by:

$$C_{Actual} = \frac{M_3 - M_2}{M_2 - M_1}, g/L \quad (3)$$

Additionally, to perform the drying extracts of solutions, a MilliQ water sample should also be present for the test accuracy.

### Dynamic Surface and Interfacial Tensions

The Du Noüy Ring Method was used to measure the surface and interfacial tension forces. The laboratory apparatus is a dynamic tensiometer acquired from Interfacial Technology Concept (Longessaigne, France).<sup>7</sup> In the Du Noüy Ring Method, the instrumental and yet fragile tool is a platinum ring kept in a wood jar when not used. The ring is submersed in the sample solution. As the test starts, the ring is being pulled out of the liquid, the surface or interfacial tension force needed is accurately recorded.

Glass cups were cleaned with MilliQ water and acetone in the sample preparation stage. For every type of polymers, 20 mL of each concentration were filled in the cups. Given the fact that the surface and interfacial tension measurements usually could not be finished by the end of the day, the sample cups were sealed by Parafilm and stored in the

fridge overnight if needed. However, when the sample were taken out from the fridge for tests, they should be placed in the fume hood with the air circulating about twenty minutes until the samples reached room temperature.

To begin the surface and interfacial tension measurements, the water circulation should be opened first and set to 25 °C. In order to keep the system at this constant temperature, around 50 mL of MilliQ water should be filled in the sample cave of the apparatus. The first sample to be tested should always be MilliQ water to calibrate the tensiometer. Place the sample cup in the middle of the sample cave. The ring was hooked up but not in contact with solution after the sample cup was ready.

For surface tension measurements, the ring was submersed into the liquid once it was stable in the air and the weight was adjusted to 0.000 g. However, for the interfacial tension measurements, the sample cup containing only the “heavier” (larger density) solution was placed in the cave first. Once the ring was submersed in the first liquid, the “lighter” (smaller density) liquid was injected in by pipettes. In the study, the Nujol oil was used during the whole time, and the density of the oil used was smaller than MilliQ water and sample solutions. Although it was suggested in the manual that the lighter solution should have about one third to half in height of the heavier solution, the surface-active properties of modified dextran were not quite predictable. Therefore, a half to two thirds in height is suggested here based on the practical experience and users’ judgment.

An important parameter in the surface and interfacial tension force measurement is the wait time. After the ring was submersed in the liquid or sub-liquid, the sample should



be kept still for a period of time for the surfactants to reach the liquid level. Typically, wait time of native dextran was twenty minutes, and that of other modified dextran was 40 minutes to an hour.

Last but not least, the surface and interfacial tension tests were subtle and important lab work in the project study. Therefore, it is important to repeat the same experiment for the result validation.

## Results and Discussion

### Viscometry

#### Native Dextran

Flow Time (seconds)	MilliQ Water	Native Dextran				
		Concentration, g/L				
		5	10	20	40	60
	86.22	106.89	150.69	165.17	215.63	407.48
	86.22	106.99	152.33	165.86	217.06	408.83
	86.24	107.02	152.75	166.30	217.19	409.14
	86.36	107.06	152.81	166.31	217.22	409.27
	86.78	107.07	152.85	166.47	217.26	409.34
	86.79	107.27	152.88	166.63	217.32	409.68
	86.80	107.43	152.99	166.68	217.44	410.16
	86.85	107.48	153.17	166.72	217.61	411.97
Average	<b>86.53</b>	<b>107.14</b>	<b>152.77</b>	<b>166.38</b>	<b>217.25</b>	<b>409.40</b>
$\eta$ L/g		<b>0.048</b>	<b>0.077</b>	<b>0.046</b>	<b>0.038</b>	<b>0.062</b>

Table 1: Viscosity - Native Dextran

The flow time results of MilliQ water and native dextran solutions at different concentrations were collected in Table 1, and the corresponding specific viscosity,  $\eta_{sp}$ , in L/g, was calculated as well.

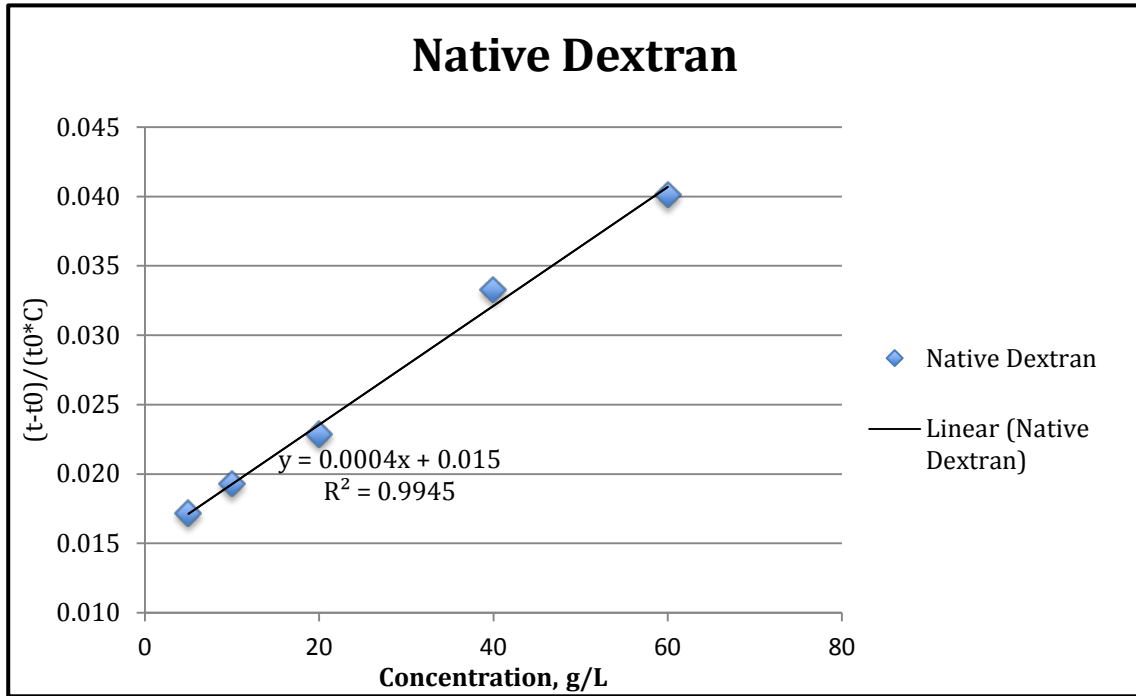


Figure 9: Huggins' Constant - Native Dextran

The linear relationship between  $\eta_{sp}$  and concentration was derived from the scatter chart (see Figure 9), and it was found to be  $y = 0.0004x + 0.015$ ,  $a = 0.0004$ ,  $b = 0.015$ .

Therefore,  $k_H$  was found by the equation:

$$k_H = \frac{0.0004}{0.015^2} = 1.778$$

Huggins' constant was found to be close to 0.5. This Huggins' coefficient is a higher number than the found value. However, it is within the acceptable range of 0.4 – 2.

Flow Time (seconds)	MilliQ Water	Modified Dextran DexC10 <sub>7</sub>				
		Concentration, g/L				
		5	10	20	40	60
	85.07	89.68	95.08	114.80	175.37	346.23
	85.07	89.70	95.08	114.84	175.98	347.02
	85.08	89.70	95.09	114.85	175.99	347.28
	85.09	89.70	95.09	114.85	176.08	347.29
	85.09	89.70	95.09	114.86	176.15	347.53
	85.10	89.70	95.09	114.86	176.17	348.20
	85.10	89.71	95.10	114.88	176.21	348.21
	85.13	89.76	95.11	114.91	176.24	348.40
Average	<b>85.09</b>	<b>89.70</b>	<b>95.09</b>	<b>114.86</b>	<b>176.10</b>	<b>347.59</b>
$\eta$ L/g		<b>0.011</b>	<b>0.012</b>	<b>0.017</b>	<b>0.027</b>	

Table 2: Viscosity - DexC10<sub>7</sub>

The flow time results of MilliQ water and modified dextran DexC10<sub>7</sub> solutions at different concentrations were collected in Table 2, and the corresponding specific viscosity,  $\eta_{sp}$ , was calculated as well. The viscosity of DexC10<sub>7</sub> is a lot less than that of the native dextran T40. Therefore, by modifying the native dextran, a more surface-active surfactant was obtained.

The linear relationship between  $\eta_{sp}$  and concentration was derived from the scatter chart trendline at the order of 1 (see Figure 10), and it was found to be  $y = 0.0005x + 0.0079$ ,  $a = 0.0005$ ,  $b = 0.0079$ . Therefore,  $k_H$  was found by the equation:

$$k_H = \frac{0.0005}{0.0079^2} = 8.012$$

Huggins' constant of DexC10<sub>7</sub> is bigger than 5. This finding is consistent with the expectation that Huggins' constant can reach high above 5 for highly interacting macromolecules.

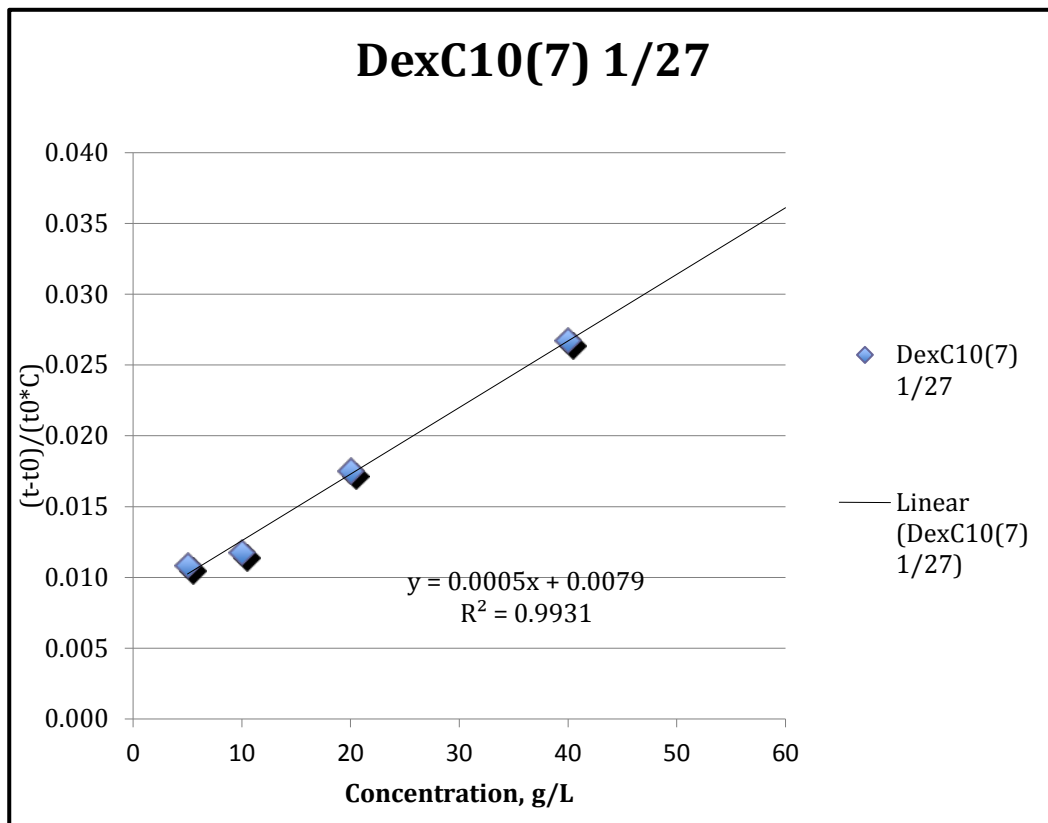


Figure 10: Huggins' Constant - DexC10<sub>7</sub>

## Surface Tension

The surface tensions of MilliQ water and modified dextran were measured and collected to compute and compare the surface-active properties of the polymers. The first surface tension data for DexC10<sub>7</sub> was plotted in Figure . However, the trendline of the plotted data was not as expected.

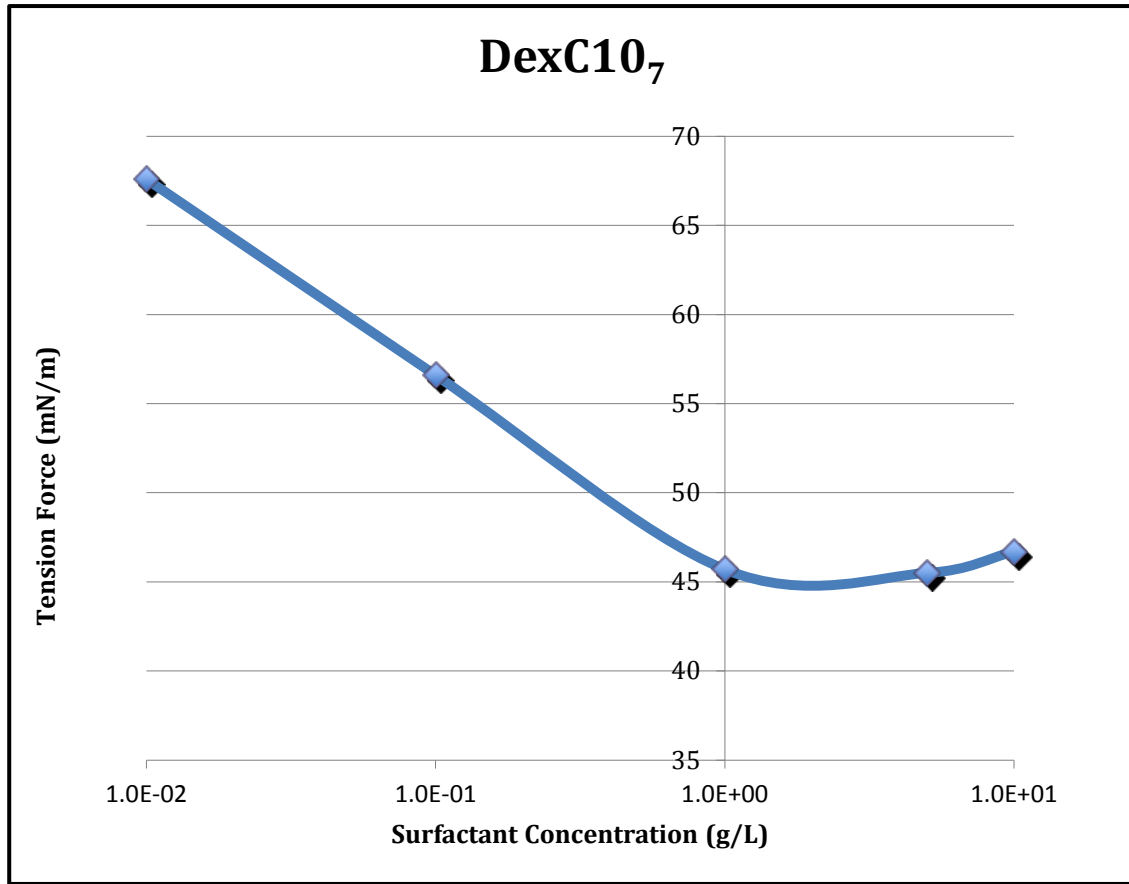


Figure 11: Surface Tension - DexC10<sub>7</sub>

It was then found out that the wait time (twenty minutes) for DexC10<sub>7</sub> was not long enough for the surfactants to move up to the liquid surface, especially for the low concentration samples. To get the best performance wait time, an analytical surface tension measurement was performed. The surface tension measurement was taken at four different wait time (twenty minutes, forty minutes, one hour, two hours). The results were collected and listed in Figure 11.

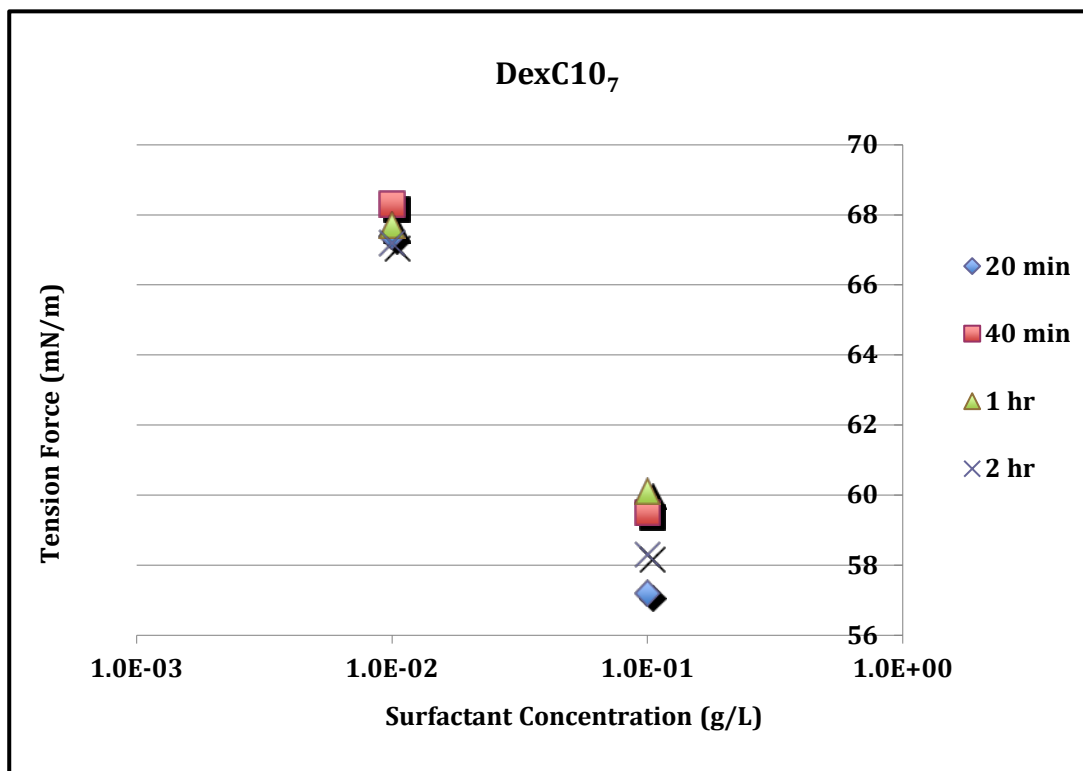


Figure 12: Surface Tension with Different Induction Period - DexC10<sub>7</sub>

Compared with other longer wait times, the twenty minutes wait time used in the past showed lower tension forces which might result from the insufficient retention time for surfactants. However, the wait time of two hours was off the track too. It was believed that due to this long wait time, some surfactants were no longer surface-active any more. Based on the listed results, the wait time for DexC10<sub>7</sub> was decided to be either forty minutes or one hour. For the future reference, the wait time for other modified dextran was either forty minutes or one hour based on the concentration of solution. It would be forty minutes for concentrated solution (>1 g/L) and one hour for diluted solution (<1 g/L).

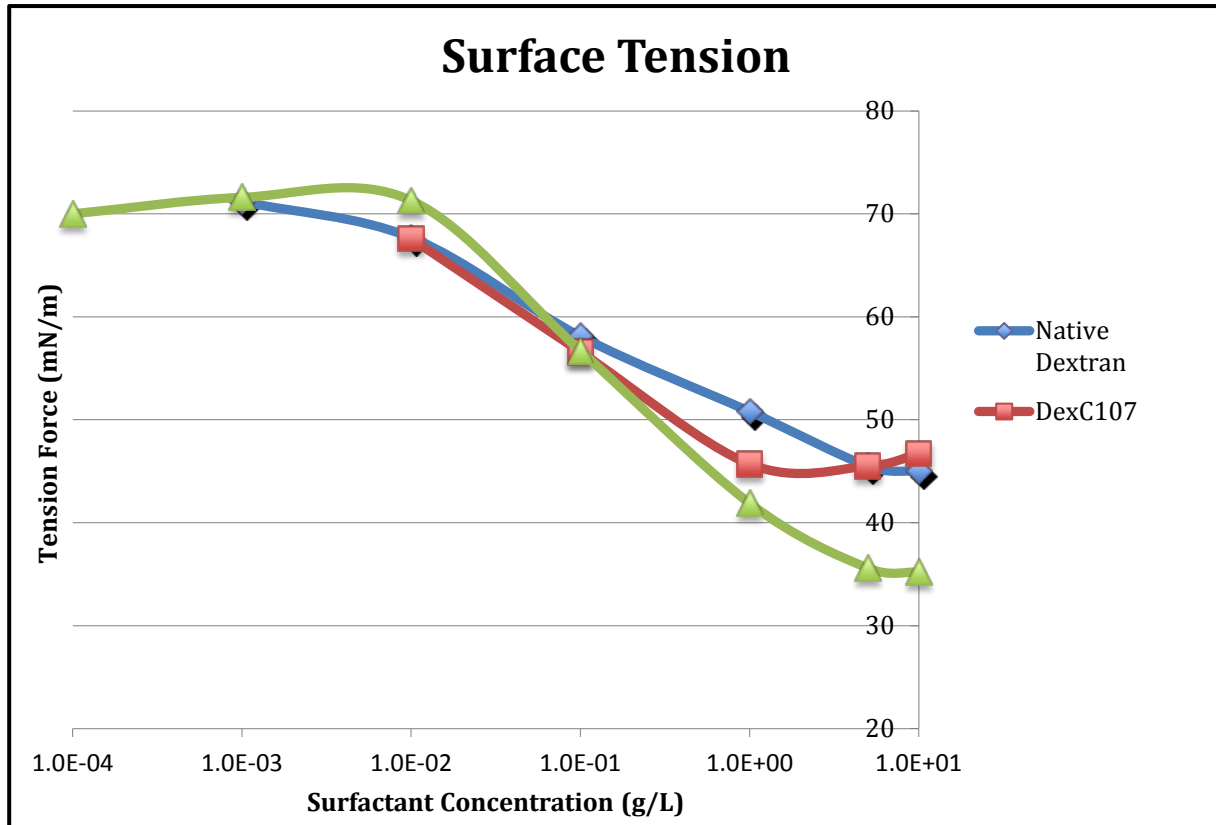


Figure 13: Surface Tension Summary

According to the surface tension data plotted on the graph, the surface active properties of different polymers were close at lower concentrations ( $<0.1$  g/L) and they differ at higher concentrations ( $>0.1$  g/L). At the concentration of 0.1 g/L, the three trend lines nearly intersect with each other with a tension force of approximately 56.6 mN/m.

However, the behavior of three polymers followed a certain pattern. At the concentration higher than 0.01 g/L, the trend lines were flat, which means slight changes over concentration. In the concentration range from 0.01 to 5 g/L, the trend lines were steep. The surface tension force dropped significantly as the concentration increases in the range. When the concentration was higher than 5 g/L, the trend lines had very small slope. Even though the data acquired might not be sufficient enough to illustrate the flat trendline,



the points plotted in the figure presented a much lower tension force dropping rate.

Therefore, the trend lines of concentration higher than 5 g/L could be predicted as a flat line with a very small slope.

### Interfacial Tension

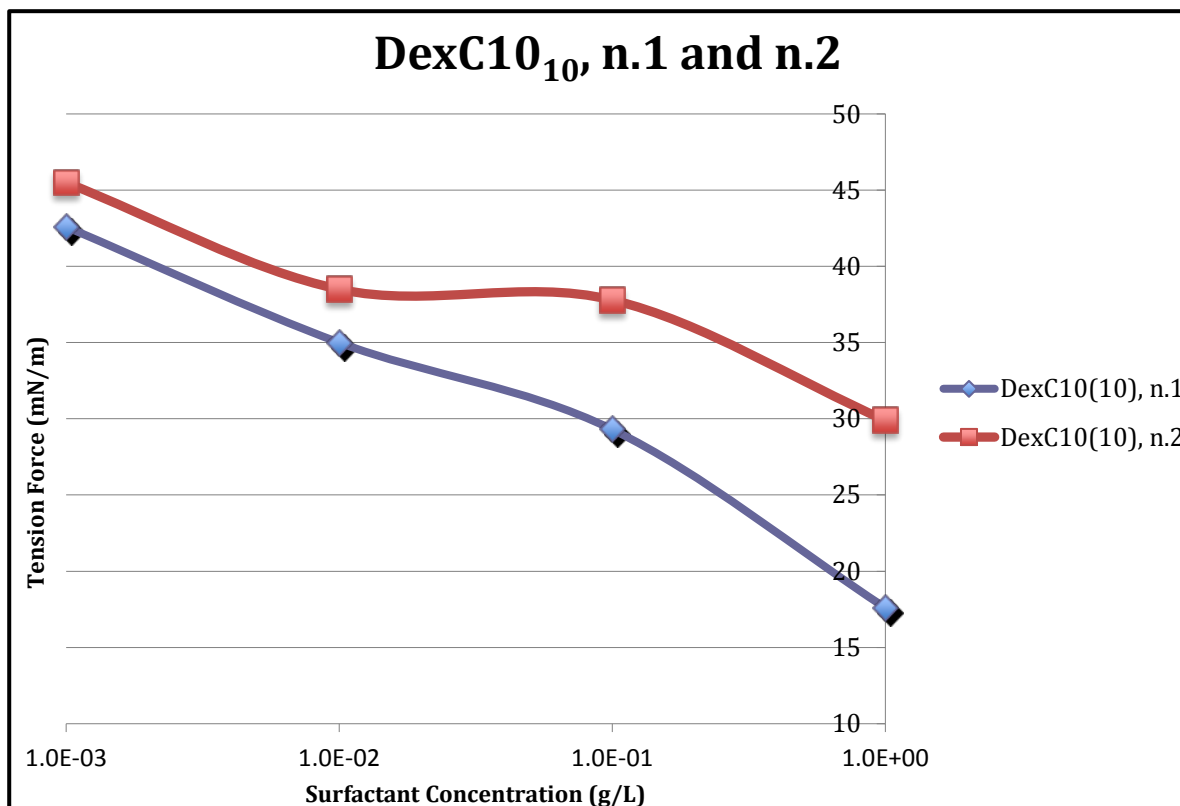


Figure 14: Interfacial Tension - DexC10<sub>10</sub>, n°, and n°2

The interfacial tension test results were plotted in Figure 14. In the graph, DexC10<sub>10</sub> n°2 demonstrated a larger interfacial tension force at all concentrations. It has been studied that the densely grafted C10 groups favor intramolecular aggregates formation rather than oil-water interface adsorption.<sup>5</sup> The reason for the variance between n°1 and n°2 was the initial dextran modification process.

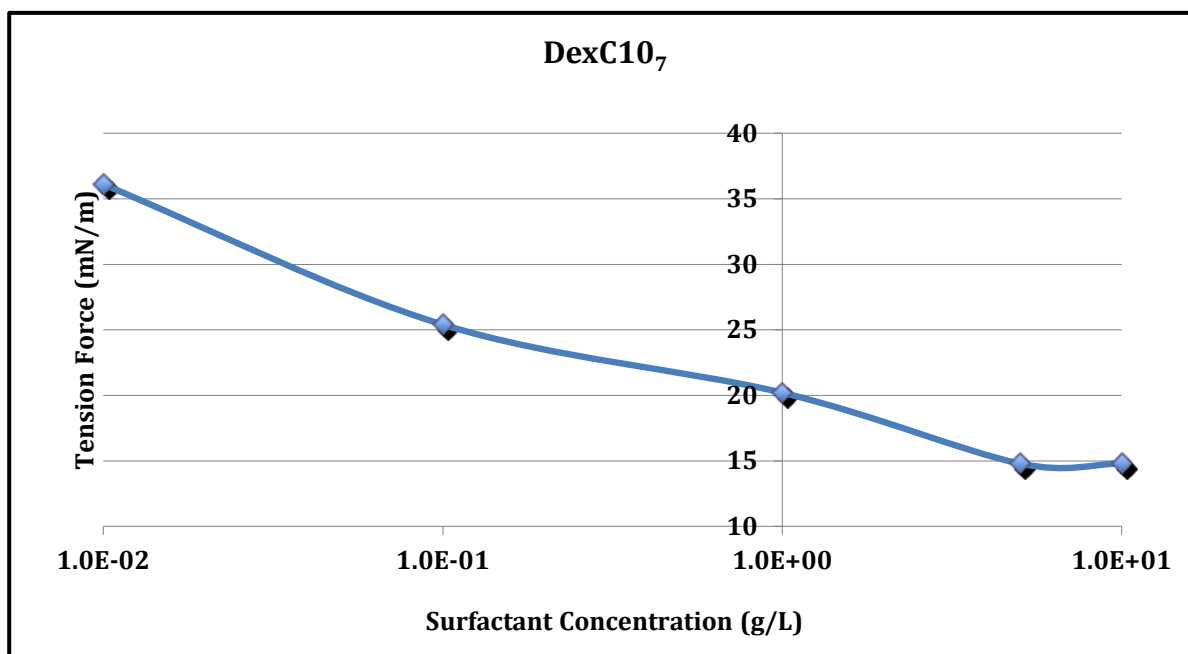


Figure 15: DexC10<sub>7</sub> - Interfacial Tension

On the other hand, the interfacial tension forces of DexC10<sub>7</sub> (Figure 15) were smaller than those of DexC10<sub>10</sub>. In the previous studies from LCPM, it was known that for DexC10<sub>γ</sub> derivatives, as  $\gamma$  increases, the interfacial tension force decreases correspondingly. A short list of samples is listed in Table 3.

Polymer	$\gamma_i$ (mN/m)
T40©	52.8 <sup>c</sup>
DexC6 <sub>12</sub>	14
DexC6 <sub>21</sub>	8
DexC6 <sub>38</sub>	3
DexC10 <sub>11</sub>	15.5
DexC10 <sub>24</sub>	10.5
DexC10 <sub>31</sub>	8

Table 3: Sample Modified Dextran Properties<sup>8</sup>

## Dry Extracts of the Solution

The solution samples were prepared by basic sample preparation techniques including the use of balance scale, pipettes, and other analytical laboratory tools. Despite how carefully the sample preparation was handled, the random error was still inevitable. Thus, the dry extracts of the solution was performed in order to get the correct concentration of the samples.

The dry extracts of the solution results for DexC10<sub>7</sub> flow time measurement are listed in Table 4. The actual concentrations were calculated using the equation  $c = \frac{m_2 - m_1}{m_1 - m_0}$

Flow Time (seconds)	MilliQ Water	Modified Dextran DexC10 <sub>7</sub>				
		Concentration, g/L				
		4.08978422	8.31395815	16.4927539	34.8380765	55.9564948
	85.07	89.68	95.08	114.80	175.37	346.23
	85.07	89.70	95.08	114.84	175.98	347.02
	85.08	89.70	95.09	114.85	175.99	347.28
	85.09	89.70	95.09	114.85	176.08	347.29
	85.09	89.70	95.09	114.86	176.15	347.53
	85.10	89.70	95.09	114.86	176.17	348.20
	85.10	89.71	95.10	114.88	176.21	348.21
	85.13	89.76	95.11	114.91	176.24	348.40
Average	85.09	89.70	95.09	114.86	176.10	347.59
(t-t <sub>0</sub> )/(t <sub>0</sub> *C) L/g		0.013	0.014	0.021	0.031	

Table 4: Dry Extracts of the Solution

Since the original ideal concentration of native dextran samples were 5, 10, 20, 40, 60 g/l respectively, the actual concentrations were very close to the ideal ones. The concentrations of solution samples are essential for the subtle emulsion system involved in this project study.

## Conclusion and Recommendations

In the research project, polymeric surfactants were prepared by modifying the native dextran T40. The functional group  $n\text{-C}_{10}\text{H}_{21}$ - (C10) was grafted onto the backbone of the dextran by two different processes: oil-in-water emulsion solvent evaporation method and solvent diffusion method. The experimental study fulfilled the mission of the project by (1) deriving the values of Huggins' constant for both native dextran and dextran derivative (DexC10<sub>7</sub>); (2) comparing surface and interfacial tension of various dextran derivatives; (3) identifying the effect of the different modification processes of the same dextran derivative.

The polymer solution behavior was examined by viscometric experiments, and Huggins' constant was derived. Huggins' constant is approximately around 0.4 in general for non-interacting macromolecules in good solvent, and it could be higher than 5 for highly interacting macromolecules. For native dextran T40 in water, the Huggins' constant was in good agreement with the model. For modified polysaccharide DexC10<sub>7</sub>, the Huggins' constant reached the value as high as 8. Such high Huggins' constant of dilute polymer solution could be attributed to the hydrogen bonds between -OH groups. In addition, at such high values, the uncertainty of Huggins' constant made it unlikely to compare with other polymers nor to comment any further.

Polymer	Aqueous Medium	C, g/L	K <sub>H</sub>	Surface Tension, mN/m	Interfacial Tension, mN/m
T40	Water	5	1.778	45	N/A
DexC10 <sub>5</sub>	Water	5	N/A	35.6	N/A
DexC10 <sub>7</sub>	Water	5	8.012	45.5	
		1			20.2
DexC10 <sub>10</sub> , n°1	Water	1	N/A	N/A	17.6
DexC10 <sub>10</sub> , n°2	Water	1	N/A	N/A	29.9

**Table 5: Summary of Final Results for Dextran and Dextran Derivatives**

The surface-active properties were studied at both air-water interface and oil-water interface. Both surface and interfacial tension forces were concerned with the surface-active properties. Overall, the native dextran and dextran derivatives all followed the surface / interfacial tension force model as expected. Native dextran and DexC10<sub>7</sub>, DexC10<sub>5</sub> shared similar surface-active properties in terms of surface tension. On the other hand, the interfacial tension forces of DexC10<sub>10</sub> (n°1) and DexC10<sub>7</sub> were close, which indicated that these polymers shared similar surface-active property.

However, even DexC10<sub>10</sub> (n°1) and DexC10<sub>10</sub> (n°2) were identical in chemical structure and substitution ratio, these polymers behaved differently in the aqueous media. DexC10<sub>10</sub> (n°2) was less surface-active in the aqueous solution. The only difference between DexC10<sub>10</sub> (n°1) and DexC10<sub>10</sub> (n°2) was the modification process. In conclusion, the biphasic medium diffusion modification process would make the polymer less surface

active, and the freeze-drying modification process would make the polymer more surface-active.

The kinetics of interfacial tension decrease was especially important. Due to the time constraints, it was not included in this project scope. Theoretically, the interfacial tension decrease could be slower than that of molecular homologues.<sup>9</sup> This interfacial tension decrease could be plotted over a long period of time by an empirical equation suggested by Hansen<sup>9</sup> which was usually used to calculate the asymptotic value of the interfacial tension:

$$\gamma_i(t) = \gamma_{ie} + \frac{A}{\sqrt{t}} \quad (4)$$

In Equation (4),  $t$  = time,  $\gamma_{ie}$  = interfacial tension force (N/m),  $A$  = empirical constant ( $s^{1/2}$ ).

An interesting finding during the surface / interfacial tension force experiments was the wait time of diluted polymer solutions (<1 g/L) should be longer than concentrated solutions ( $\geq 1$  g/L). For dilute polymer solutions, the surface / interfacial tension measurement should start an hour after the solution placed in the sample vessel of the tensiometer. This is called the induction period for the macromolecules to adsorb. The induction period should be long enough to get detectable effect.<sup>9</sup> The induction period used for diluted polymer solutions were 40 min to 1 hr, and 20 min for concentrated solutions. The longer induction period was probably due to the high hydrophobicity of the C10 group which easily led to the formation of polymeric aggregates.<sup>9</sup>

However, the ultimate goal of understanding the behavior and influence of the amphiphilic polysaccharides was to relate the oil-in-water interfacial tension to the chemical structure. Thus, this project should be followed by a droplet sizing study and the stability of the oil-in-water emulsions. The modified polysaccharides would eventually be used as emulsion stabilizers in various processes to create colloidal systems. The surface characteristics of the polymers should be included in the future study as well.



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## Appendix

### Appendix.1 Du Noüy Ring Method Protocol

#### Measuring the Surface Tension

1. Move the sample stage downward.
2. Suspend the cleaned ring from the hook at the force sensor.
3. Turn on the tensiometer.
4. Fill the sample to be measured into the sample vessel and the vessel on the sample stage.
5. Select “Du Noüy Ring” in the main menu.
6. Check and adapt the current parameters.
7. Move the sample stage upward until the ring is located just above the liquid surface.  
Wait till the ring no longer moves about and the liquid has come to rest.
8. Press “Tare” to calibrate the weight of the ring in air. Wait till a weight of 0.0000 g is indicated on the display.
9. Move the sample stage upward and immerse the ring about 1 mm deep in the liquid.
10. Press “start” to measure the surface tension of the liquid.

The tensiometer operates automatically. During the measurement five individual surface tension values will be given. After five tests, the mean value for the interfacial tension and the standard deviation will be given.

#### Measuring the Interfacial Tension

1. Move the sample stage downward.

2. Suspend the cleaned ring from the hook at the force sensor.
3. Turn on the tensiometer.
4. Fill the sample to be measured into the sample vessel and the vessel on the sample stage.
5. Check and adapt the current parameters.
6. Move the sample stage upward until the ring is immersed into the light phase. The immersion depth should be the same as for the later measurement. Wait till the liquid has come to rest.
7. Press "Tare" to calibrate the weight of the ring in air. Wait till a weight of 0.0000 g is indicated on the display.
8. Move the sample stage downward and remove the sample vessel filled with the light phase. Remove the ring from the hook and clean it (including heating to red heat). Then suspend the plate again.
9. Fill a clean sample vessel to one third with the heavy phase and place it on the sample stage.
10. Move the sample table upward so that the ring is immersed 2 – 3 mm into the heavy phase. Wait until the liquid has come to rest.
11. Carefully overlay the heavy phase with the lighter phase. The filling level depends on the immersion depth of the ring during the previous taring procedure.
12. Press "start" to measure the interfacial tension between the liquids.



The tensiometer operates automatically. During the measurement five individual surface tension values will be given. After five tests, the mean value for the interfacial tension and the standard deviation will be given.

## Appendix 2. Experimental Results

### 2.1 Viscometry – Native Dextran – Ideal Concentration

Flow Time (seconds)	MilliQ Water	Native Dextran				
		Concentration, g/L				
		5	10	20	40	60
	86.22	106.89	150.69	165.17	215.63	407.48
	86.22	106.99	152.33	165.86	217.06	408.83
	86.24	107.02	152.75	166.30	217.19	409.14
	86.36	107.06	152.81	166.31	217.22	409.27
	86.78	107.07	152.85	166.47	217.26	409.34
	86.79	107.27	152.88	166.63	217.32	409.68
	86.80	107.43	152.99	166.68	217.44	410.16
	86.85	107.48	153.17	166.72	217.61	411.97
Average	<b>86.53</b>	<b>107.14</b>	<b>152.77</b>	<b>166.38</b>	<b>217.25</b>	<b>409.40</b>
$\eta$ L/g		<b>0.048</b>	<b>0.077</b>	<b>0.046</b>	<b>0.038</b>	<b>0.062</b>

## 2.2 Viscometry – DexC10<sub>7</sub> – Ideal Concentration

Flow Time (seconds)	MilliQ Water	Modified Dextran DexC10 <sub>7</sub>				
		Concentration, g/L				
		5	10	20	40	60
	85.07	89.68	95.08	114.80	175.37	346.23
	85.07	89.70	95.08	114.84	175.98	347.02
	85.08	89.70	95.09	114.85	175.99	347.28
	85.09	89.70	95.09	114.85	176.08	347.29
	85.09	89.70	95.09	114.86	176.15	347.53
	85.10	89.70	95.09	114.86	176.17	348.20
	85.10	89.71	95.10	114.88	176.21	348.21
	85.13	89.76	95.11	114.91	176.24	348.40
Average	<b>85.09</b>	<b>89.70</b>	<b>95.09</b>	<b>114.86</b>	<b>176.10</b>	<b>347.59</b>
$(t-t_0)/(t_0 \cdot C)$ L/g		<b>0.011</b>	<b>0.012</b>	<b>0.017</b>	<b>0.027</b>	

## 2.3 Dry Extract Solution Results

Sample Label		Ideal Concentration, g/L	Empty Bottle, g	Solution g	Dried Extracts+ Bottle, g	Actual Conc, g/L
1	DexC10 <sub>7</sub>	5	8.20347	1.15165	8.20818	4.08978
2		10	8.28113	1.2473	8.2915	8.31396
3		20	12.3801	1.06471	12.39766	16.4928
4		40	12.16652	1.26356	12.21054	34.8381
5		60	8.21514	1.27617	8.28655	55.9565
6	Native Dextran T40	5	8.18975	1.1204	8.19477	4.48054
7		10	8.16887	1.15182	8.17894	8.74269
8		20	12.74902	1.5702	12.77765	18.2333
9		40	8.12263	1.13858	8.16266	35.1578
10		60	8.24455	1.19238	8.30992	54.8231
1	DexC10 <sub>7</sub>	0.01	8.2854	1.05113	8.28458	
2		0.1	12.30172	1.09335	12.30014	
3		MilliQ	13.02917	1.01849	13.02852	

## 2.4 Viscometry – DexC10<sub>7</sub> – Actual Concentration

Flow Time (seconds)	MilliQ Water	Modified Dextran DexC10 <sub>7</sub>				
		Concentration, g/L				
		4.08978422	8.31395815	16.4927539	34.8380765	55.9564948
	85.07	89.68	95.08	114.80	175.37	346.23
	85.07	89.70	95.08	114.84	175.98	347.02
	85.08	89.70	95.09	114.85	175.99	347.28
	85.09	89.70	95.09	114.85	176.08	347.29
	85.09	89.70	95.09	114.86	176.15	347.53
	85.10	89.70	95.09	114.86	176.17	348.20
	85.10	89.71	95.10	114.88	176.21	348.21
	85.13	89.76	95.11	114.91	176.24	348.40
Average	<b>85.09</b>	<b>89.70</b>	<b>95.09</b>	<b>114.86</b>	<b>176.10</b>	<b>347.59</b>
$(t-t_0)/(t_0 \cdot C)$ L/g		0.013	0.014	0.021	0.031	

## 2.5 Surface Tension – Native Dextran

Concentration, g/L	1	2	3	4	5	St-Dev, mN/m	IFT, mN/m
MilliQ	68.7	69.1	68.6	68.6	68.6	0.2	68.7
MilliQ	71.7	71.7	71.8	71.8	71.8	0.1	71.8
1.0E-03	71.4	71.3	70.9	70.9	71.3	0.3	71.2
1.0E-02	70.7	70.2	70.2	70.1	70	0.3	70.2
1.0E-02	68.2	67.8	67.6	67.5	67.4	0.3	67.7
1.0E-01	59	58.4	58	57.7	57.7	0.5	58.1
1.0E+00	51.5	50.9	50.9	50.4	50.4	0.4	50.8
5.0E+00	46.2	45.8	45.4	45.2	45.2	0.5	45.5
1.0E+01	45.5	45.2	44.9	44.6	44.8	0.4	45

## 2.6 Surface Tension – DexC10<sub>7</sub>

Concentration, g/L	1	2	3	4	5	St-Dev, mN/m	IFT, mN/m
MilliQ	71.9	71.8	72.1	71.9	72.2	0.2	72
MilliQ	71.7	72.1	72	71.8	72	0.2	71.9
1.0E-02	67.9	67.5	67.4	67.6	67.5	0.2	67.6
1.0E-01	57.3	56.9	56.5	56.2	56.2	0.5	56.6
1.0E+00	46.5	45.9	45.5	45.5	45.3	0.5	45.7
5.0E+00	46.2	45.8	45.4	45.2	45.2	0.5	45.5
1.0E+01	47.2	46.8	46.6	46.5	46.4	0.3	46.7

## 2.7 Surface Tension – DexC10<sub>7</sub> – 2

Concentration, g/L	1	2	3	4	5	St-Dev, mN/m	IFT, mN/m	Wait Time
MilliQ	70.5	70	69.8	70	70.1	<b>0.3</b>	<b>70.1</b>	N/A
MilliQ	70.9	70.3	70.7	70.5	70.7	<b>0.2</b>	<b>70.6</b>	N/A
MilliQ	71.2	71.4	71.5	71.2	71.5	<b>0.2</b>	<b>71.4</b>	N/A
1.0E-02	67.7	67.5	67.4	67.1	67.2	<b>0.2</b>	<b>67.4</b>	20 min
1.0E-02	68.3	68.4	68.3	68.2	68.2	<b>0.1</b>	<b>68.3</b>	40 min
1.0E-02	67.9	67.9	67.8	67.8	67.3	<b>0.2</b>	<b>67.7</b>	1 hr
1.0E-02	67.1	67.3	67.2	67.2	67.1	<b>0.1</b>	<b>67.2</b>	2 hr
1.0E-01	58	57.4	57	56.9	56.8	<b>0.5</b>	<b>57.2</b>	20 min
1.0E-01	60.2	59.7	59.3	59.2	59	<b>0.5</b>	<b>59.5</b>	40 min
1.0E-01	60.9	60.2	60	59.8	59.6	<b>0.5</b>	<b>60.1</b>	1 hr
1.0E-01	58.8	58.7	58.2	58.1	57.9	<b>0.4</b>	<b>58.3</b>	2 hr

## 2.8 Surface Tension – DexC10<sub>5</sub>

Concentration, g/L	1	2	3	4	5	St-Dev, mN/m	IFT, mN/m
MilliQ	72.7	72	72.3	72.2	72.7	<b>0.2</b>	<b>72</b>
1.0E-04	70.3	69.8	70	69.9	69.9	<b>0.2</b>	<b>70</b>
1.0E-03	71.4	71.7	71.7	71.7	71.3	<b>0.2</b>	<b>71.6</b>
1.0E-02	71.6	71.5	71.2	71	71.1	<b>0.3</b>	<b>71.3</b>
1.0E-01	57.4	56.8	56.6	56.4	56.5	<b>0.4</b>	<b>56.7</b>
1.0E+00	43.4	42.2	41.5	41.4	41.2	<b>0.9</b>	<b>41.9</b>
5.0E+00	36.1	35.6	35.6	35.5	35.2	<b>0.3</b>	<b>35.6</b>
1.0E+01	35.3	35.3	35.2	35.1	35.2	<b>0.1</b>	<b>35.2</b>

## 2.9 Interfacial Tension – DexC10<sub>7</sub>

Concentration, g/L	1	2	3	4	5	St-Dev, mN/m	IFT, mN/m
MilliQ	46.5	46.2	46.2	46.1	46.1	0.1	46.2
1.0E-02	36.4	36.2	36.1	36	36	<b>0.2</b>	<b>36.1</b>
1.0E-01	26	25.5	25.3	25	24.9	<b>0.5</b>	<b>25.4</b>
1.0E+00	20.8	20.2	20	19.9	19.9	<b>0.4</b>	<b>20.2</b>
5.0E+00	15.6	14.4	15	14.1	14.7	<b>0.6</b>	<b>14.8</b>
1.0E+01	15.5	14.4	14.9	14.8	14.7	<b>0.4</b>	<b>14.8</b>

## 2.10 Interfacial Tension – DexC10<sub>7</sub> – 2

Concentration, g/L	1	2	3	4	5	St-Dev, mN/m	IFT, mN/m	Wait Time
MilliQ	71.2	71.4	71.5	71.2	71.5	0.2	<b>71.4</b>	N/A
1	18.1	16.1	17.5	16.5	17.2	0.8	<b>17</b>	1 hr
10	15.6	14.5	14.9	14.2	14.7	0.5	<b>14.8</b>	20 min

## 2.11 Interfacial Tension – DexC10<sub>10</sub> (n°1)

Concentration, g/L	1	2	3	4	5	St-Dev, mN/m	IFT, mN/m
MilliQ Surface	70.7	70.4	70.7	70.9	70.9	<b>0.2</b>	<b>70.7</b>
MilliQ Interfacial	46.5	46.2	46.2	46.1	46.1	<b>0.1</b>	<b>46.2</b>
1.0E-03	43	42.7	42.6	42.4	42.3	<b>0.3</b>	<b>42.6</b>
1.0E-02	35.6	35.2	34.8	34.8	34.6	<b>0.4</b>	<b>35</b>
1.0E-01	30.1	29.5	29.2	28.9	28.8	<b>0.5</b>	<b>29.3</b>
1.0E+00	18.3	17.8	17.5	17.3	17.2	<b>0.4</b>	<b>17.6</b>



### 2.12 Interfacial Tension – DexC10<sub>10</sub> (n°1) – 2

Concentration, g/L	1	2	3	4	5	St-Dev, mN/m	IFT, mN/m
MilliQ Surface	72.5	72.3	72.5	72.1	72.5	0.2	72.4
MilliQ Interfacial	46.4	45.7	45.6	46.2	46	0.3	46
1.0E-03	37.8	37.3	37.1	36.9	36.8	0.4	37.2
1.0E-02	35.6	35.2	34.8	34.8	34.6	0.4	35
1.0E-01	29.4	29.1	28.9	28.8	28.6	0.3	29
1.0E+00	23	22.1	21.7	21.3	21.2	0.7	21.9

### 2.13 Interfacial Tension – DexC10<sub>10</sub> (n°1) – 3

Concentration, g/L	1	2	3	4	5	St-Dev, mN/m	IFT, mN/m
MilliQ Surface	72.1	71.8	72.1	71.7	72.1	0.2	71.9
MilliQ Interfacial	42.1	41.5	41.2	40.8	40.7	0.6	41.3
1.0E-04	34.6	34.2	34	33.9	33.8	0.3	34.1
1.0E-03	35.6	35.2	34.8	34.8	34.6	0.4	35
1.0E-02	31.6	31.3	31	30.9	30.7	0.3	31.1
1.0E-01	26.3	25.8	25.5	25.3	25.2	0.4	25.6
1.0E+00	23	22.1	21.7	21.3	21.2	0.7	21.9

## 2.14 Interfacial Tension – DexC10<sub>10</sub> (n°2)

Concentration, g/L	1	2	3	4	5	St-Dev, mN/m	IFT, mN/m
MilliQ Surface	71.9	71.9	72	71.9	72	0	71.9
MilliQ Interfacial	46.5	46.2	46.2	46.1	46.1	0.1	46.2
1.0E-03	45.7	45.6	45.4	45.4	45.4	0.1	45.5
1.0E-02	39.1	37.9	38.5	38.5	38.3	0.4	38.5
1.0E-01	38.1	37.9	37.7	37.7	37.5	0.2	37.8
1.0E+00	29.1	33	31.1	28.6	27.7	2.1	29.9

## 2.15 Interfacial Tension – DexC10<sub>10</sub> (n°2) – 2

Concentration, g/L	1	2	3	4	5	St-Dev, mN/m	IFT, mN/m
MilliQ Surface	71.9	72.4	72.2	72.4	72.4	0.2	72.3
MilliQ Interfacial	46.4	46.1	46	46	46	0.2	46.1
1.0E-03	43	42.7	42.6	42.4	42.3	0.3	42.6
1.0E-02	39.1	37.9	38.5	38.5	38.3	0.4	38.5
1.0E-01	39.3	39.1	39	38.9	39	0.2	39.1
1.0E+00	34.5	34	33.7	33.5	33.3	0.5	33.8

## 2.16 Interfacial Tension – DexC10<sub>10</sub> (n°2) – 3

Concentration, g/L	1	2	3	4	5	St-Dev, mN/m	IFT, mN/m
MilliQ Surface	72.1	72.1	71.6	72	72	0.2	72
MilliQ Interfacial	46.4	46.1	46	46	46	0.2	46.1
1.0E-04	37.3	36.8	36.5	36.4	36.4	0.4	36.7
1.0E-03	33.6	32.9	32.7	32.5	32.3	0.5	32.8
1.0E-02	32.3	33.4	33.3	33.1	33.1	0.4	33.1
1.0E-01	35.3	34.9	34.8	34.6	34.6	0.3	34.8
1.0E+00	31.2	30.6	30.3	30	29.9	0.5	30.4

## 2.17 Surface Tension – DexC10<sub>5</sub>

Concentration, g/L	1	2	3	4	5	St-Dev, mN/m	IFT, mN/m
MilliQ	72.7	72	72.3	72.2	72.7	0.2	72
1.0E-04	70.3	69.8	70	69.9	69.9	0.2	70
1.0E-03	71.4	71.7	71.7	71.7	71.3	0.2	71.6
1.0E-02	71.6	71.5	71.2	71	71.1	0.3	71.3
1.0E-01	57.4	56.8	56.6	56.4	56.5	0.4	56.7
1.0E+00	43.4	42.2	41.5	41.4	41.2	0.9	41.9
5.0E+00	36.1	35.6	35.6	35.5	35.2	0.3	35.6
1.0E+01	35.3	35.3	35.2	35.1	35.2	0.1	35.2

## 2.18 Interfacial Tension – DexC10<sub>5</sub>

Concentration, g/L	1	2	3	4	5	St-Dev, mN/m	IFT, mN/m
MilliQ	46.5	46.2	46.2	46.1	46.1	0.1	46.2
1.0E-02	36.4	36.2	36.1	36	36	<b>0.2</b>	<b>36.1</b>
1.0E-01	26	25.5	25.3	25	24.9	<b>0.5</b>	<b>25.4</b>
1.0E+00	20.8	20.2	20	19.9	19.9	<b>0.4</b>	<b>20.2</b>
5.0E+00	15.6	14.4	15	14.1	14.7	<b>0.6</b>	<b>14.8</b>
1.0E+01	15.5	14.4	14.9	14.8	14.7	<b>0.4</b>	<b>14.8</b>